④

CHEMICAL
RESEARCH,
DEVELOPMENT &
ENGINEERING
CENTER

AD-A223 070

CRDEC-TR-167

WEAR METAL ANALYSIS IN ENGINE OIL BY MICROWAVE DIGESTION AND ATOMIC ABSORPTION SPECTROSCOPY

William T. Muse, Jr.

RESEARCH DIRECTORATE

May 1990

U.S. ARMY
ARMAMENT
MUNITIONS
CHEMICAL COMMAND

Aberdeen Proving Ground, Maryland 21010-5423

Disclaimer

Distribution Statement

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE
1990 May

3. REPORT TYPE AND DATES COVERED
Final, 87 Aug - 88 Jan

4. TITLE AND SUBTITLE
Wear Metal Analysis in Engine Oil by Microwave Digestion and Atomic Absorption Spectroscopy

5. FUNDING NUMBERS
PR-1C162622A552

6. AUTHOR(S)
Muse, William T., Jr.

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Cdr, CRDEC
ATTN: SMCCR-RST-E
Aberdeen Proving Ground, MD 21010-5423

8. PERFORMING ORGANIZATION REPORT NUMBER
CRDEC-TR-167

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

Digestion procedures are described for the analysis of wear metals in National Bureau of Standards (NBS) oil samples by a closed vessel microwave digestion system. Samples were analyzed by flame atomic absorption spectroscopy. Recoveries of Al, Fe, Ni, Cu, and Pb in the 300-ppm NBS oil ranged from 98 to 103% with standard deviations from 3 to 14%. This method serves as a relatively quick matrix destruction technique for the quantitation of metals in oil.

14. SUBJECT TERMS

Aluminum	Atomic absorption	Copper
Iron	Lead	Metal analysis
Microwave digestion	Nickel	Oil

15. NUMBER OF PAGES
15

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

Blank

PREFACE

The work described in this report was authorized under Project No. 1C162622A552, Smoke and Obscurants. This work was started in August 1987 and completed in January 1988. The experimental data are recorded in laboratory notebook 87-0065.

The use of trade names or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of advertisement.

Acknowledgments

The author expresses his appreciation to Maureen Diemer for providing the National Bureau of Standards Wear Metal in Oils standards used for this study.

Blank

CONTENTS

LIST OF TABLES

WEAR METAL ANALYSIS IN ENGINE OIL BY MICROWAVE DIGESTION AND ATOMIC ABSORPTION SPECTROSCOPY

1. INTRODUCTION

Wear metal analysis in used engine oil gives a good indication on the degree of engine wear over time. An increase in metals, such as iron, copper, nickel, lead, and aluminum, can indicate wear in specific engine components (i.e., rings, pistons, bearings, etc.). A variety of methods, such as solvent extraction and acid digestion, have been used to quantitatively extract these metals from oil. A more recent technique (closed vessel microwave digestion), which can extract wear metal particles quickly and efficiently, has become available.

Solvent extraction techniques are frequently used to analyze for metals in oil by extracting the oil into an organic solvent (i.e., xylene, kerosene, methyl isobutyl ketone), followed by atomic absorption (AA) analysis. This is a quick technique; however, it suffers the disadvantage of only looking at soluble metals or small wear metal particles (<1 micron) in diameter. Metallic particles larger than 1 micron, if present, are not extracted; therefore, results are not quantitative.[1]

A particle size independent determination of wear metals in engine oils must involve an acid digestion step prior to solvent extraction and analysis. Previous work by Brown et al.[1] and Kauffman et al.[2] investigated various mixes of acids and extraction solvents to determine total metals in oil. They found that oil mixed with HF/aqua regia, heated, and extracted into MIBK/isopropanol gave excellent total metal recoveries. However, these methods required the preparation of organometallic standards, which again must be acidified, heated, and solvent extracted to quantitate the oil samples. The diluted standards were only stable for 1 day.

Another particle size independent method, without solvent extraction, would involve acid matrix destruction of the oil by open vessel, hot plate digestion. Organic material is oxidized to CO_2, H_2O, and NO_x (equations 1 and 2),[3,4] and particles are chemically oxidized to soluble salts. This technique permits total metal content in oil to be determined, using aqueous solutions as standards. The disadvantage of this method is that it requires a great deal of sample manipulation and time to complete.

$$[(C_nH_{n+2}) + HNO_3 = CO_2 + NO + H_2O] \qquad (1)$$
$$[(CH_2)_n + 2HNO = CO_2 + 2NO + 2H_2O] \qquad (2)$$

A more recent matrix destruction technique (closed vessel microwave digestion) has become commercially available. Microwaves are used to internally heat sample/acid mixtures that are contained inside a closed Teflon reaction vessel. Unlike open vessel digestion, the acid-reaction times occur much faster because polar molecules, such as mineral acids and water, will absorb microwave energy so strongly that they will rapidly increase in temperature. In addition, the closed reaction vessels allow a higher boiling point of the digestion acid to be obtained.[3] For instance, nitric acid has a boiling point of 120 °C at atmospheric pressure; however, in a sealed vessel system

(@100 psig) that temperature increases to 190 °C.[3] This technique also allows nitric acid to be used more frequently for acid digestions and reduces or eliminates the requirement for using acid mixtures or strong oxidants (i.e., perchloric acid) for complete matrix destruction.

This study describes the basic microwave parameters and digestion techniques to analyze for wear metals in oil. It determines the percent recovery of the microwave digestion technique for National Bureau of Standards (NBS), Washington, DC, wear metals (Al, Fe, Cu, Ni, Pb) in oil.

2. MATERIALS AND METHODS

2.1 Apparatus.

Digestions were conducted in a microwave digestion system (Model MDS-81, CEM Corporation, Matthews, NC), equipped with turntable, exhaust system, and digestion vessels PFA, 120 mL, with pressure relief valve assembly. Metal analysis was conducted on a flame atomic absorption spectrophotometer (AAS) (Model 3030, Perkin Elmer, Norwalk, CT).

2.2 Reagents and Standards.

The specific NBS Standard Reference Materials (SRM) were Base Oil (SRM 1083), Wear-Metals in Oil 100 ppm (SRM 1084), and Wear-Metals in Oil 300 ppm (SRM 1085). Trace-metal-grade nitric acid (J. T. Baker Chemical Company, Phillipsburg, NJ) was used for the acid digestions, as well as sample/standard pH adjustment. Stock 1000-ppm metal standards (Aldrich Chemical Company, Milwaukee, WI) were used to prepare aqueous standards for AA analysis. Potassium chloride (Aldrich Chemical Company) was used as an ionization suppressant for aluminum analysis.

2.3 Dissolution Procedure.

The NBS SRM oil samples were prepared by weighing a 0.5-g quantity of each well-agitated sample into a tared Teflon digestion vessel. When adding the oil to the digestion vessel, it was important to ensure that oil was not deposited on the vessel walls. This prevented charring of samples, which could cause incomplete digestion and low element recoveries.[3] The samples were then mixed with 12 mL of nitric acid and allowed to stand (predigest) overnight. Organic samples, such as oil, produce large amounts of reaction gases (NO_2, CO_2) during the initial microwave digestion steps. A predigestion step helps to eliminate the excessive formation of these gases, which can subsequently cause uncontrolled outgassing of the samples during microwave heating.[3]

After predigestion, the digestion vessels were torqued closed (12 ft/lb) and microwave heated. To achieve uniform heating, the samples were run on a turntable at a rate of 360° per 20 sec with 100% exhaust.

The microwave heating program, established by the manufacturer (CEM Corporation), was used as a reference starting point for the sample digestion (Table 1). This program consisted of alternatively heating and cooling the digestion vessels until the oil samples were completely digested. Accumulated gases were manually vented from the digestion vessels after each heating/cooling step. Slight modifications of this program were made because uncontrolled venting of gases occurred in some samples during the early stages of microwave heating, and a complete matrix destruction was not evident in all samples at the final heating/cooling step. The modified program (Table 2) used lower power and time settings in the heating program and slightly increased the cooling time before manually venting the samples. Also, an extra heating/cooling step was added to the program.

Table 1. Microwave Heating Program (12 Vessels) CEM Corporation Procedure, Application Note OP-5.

	Program 1 (Heating)		Program 2 (Cooling)		
Step	Time (min)	Power (%)	Time (min)	Power (%)	Venting
1	6	100	2	0	Manually
2	2	100	3	0	Manually
3	6	100	3	0	Manually
4	7	100	4	0	Manually
5	8	100	4	0	Manually
6	10	100	Cool to room temp.		Manually

Table 2. Microwave Heating Program (12 Vessels) Modified Procedure.

	Program 1 (Heating)		Program 2 (Cooling)		
Step	Time (min)	Power (%)	Time (min)	Power (%)	Venting
1	5.0	95	3.0	0	Manually
2	3.0	100	4.0	0	Manually
3	5.0	100	4.0	0	Manually
4	7.0	100	4.5	0	Manually
5	7.5	100	5.0	0	Manually
6	10.0	90	5.0	0	Manually
7	10.0	85	Cool to room temp.		Manually

The percentage of microwave power used was dictated in part by the number of digestion vessels being microwaved. The referenced procedure by CEM Corporation was established for the maximum of 12 digestion vessels. Generally, 5% less microwave power was used for every two vessels less than the maximum. In other words, if 12 vessels required 100% power, then 6 vessels would require 80-85% power to achieve the same heating. The microwave heating program established for six digestion vessels is shown in Table 3.

End points of complete sample digestion were indicated by a clear yellow solution. However, upon dilution with water a white precipitate formed in some samples. The Teflon digestion vessels were rinsed with deionized water, and the samples were quantitatively transferred to volumetric flasks. Chemical adjustments for refractory metal analysis were made by adding sufficient ionization suppressant (potassium chloride) to the samples to equal 1000-ppm potassium per final volume. Samples were then diluted up to volume (usually 50 mL) and allowed to sit overnight so that undigested sample particulates could settle to the bottom of the flask to prevent the interference of particulates on AA analysis.

2.4 Atomic Absorption Analysis.

Digested NBS samples were analyzed for wear metals by flame AAS. Aluminum was analyzed by using a nitrous-oxide flame; iron, nickel, copper, and lead were analyzed by using a lean air-acetylene flame. Aqueous standards, adjusted for acid and potassium concentrations, were used to quantify the samples. Percent recovery of the method was determined by comparing the analytical concentration of the SRM samples versus their known concentration listed by the NBS.

3. RESULTS

Results of the microwave digestion technique for NBS wear metals in oil are found in Table 4 (100 ppm) and Table 5 (300 ppm). Metal levels were below detection limits for the base oil using flame analysis. The analytical sensitivity and minimum detectable concentration levels for metals in base oil are shown in Table 6. Recovery of the wear metals in oil (100 ppm) ranged from 84 to 110%. Recovery of the wear metals in oil (300 ppm) ranged from 98 to 103%.

4. DISCUSSION

The closed vessel microwave digestion technique is a quick method to analyze for a variety of metals in oil. Twelve samples can be completely digested in approximately 60-80 min. This is much shorter than previous matrix destruction techniques, such as open vessel hot plate or bomb digestion.

Observation of the samples during the initial stages of microwave heating are important to prevent uncontrolled outgassing. Because the Teflon digestion bombs are translucent, the formation of NO_x fumes can be observed. If the fumes form quickly and are dense, then the microwave power is quickly stopped. The presence of brown fumes within 2-3 min from the start of the microwave program indicates that the reaction between acid and sample is proceeding well.[3] If little or no reaction is observed, then power and time are increased by 5% until the sample shows signs of digesting.[3] Newer microwave models have an optical pressure monitor, which can greatly aid the analyst in preventing uncontrolled sample venting.

Table 3. Microwave Heating Program (6 Vessels) Modified Procedure.

Step	Program 1 (Heating) Time (min)	Program 1 (Heating) Power (%)	Program 2 (Cooling) Time (min)	Program 2 (Cooling) Power (%)	Venting
1	6	80	4	0	Manually
2	2	85	3	0	Manually
3	4	85	4	0	Manually
4	6	85	4	0	Manually
5	7	80	4	0	Manually
6	8	80	5	0	Manually
7	10	80	6	0	Manually
8	12	75	Cool to room temp.		Manually

Table 4. Recovery of Wear Metals in Oil from SRM 1084 (100 ppm) by Microwave Digestion and AA Analysis.

SRM 1084 (100 ppm)					
Element	Amount Recovered (μg/g) Mean + SD	n*	Certified Value (μg/g)	Percent Relative Error	Percent Recovery
Al	101 ± 3.5	3	98	0	103
Fe	110 ± 2.0	3	100	10	110
Ni	101 ± 4.0	4	101	0	100
Cu	102 ± 3.0	4	98	2	102
Pb	84 ± 9.0	4	(101)**	-17	84

*Number of separate digestions and analysis.
**Values in parentheses are noncertified concentrations.

Table 5. Recovery of Wear Metals in Oil from SRM 1085 (300 ppm) by Microwave Digestion and AA Analysis.

SRM 1085 (300 ppm)					
Element	Amount Recovered (μg/g) Mean ± SD	n*	Certified Value (μg/g)	Percent Relative Error	Percent Recovery
Al	296 ± 14	4	296	0	100
Fe	312 ± 6	4	300	4	103
Ni	296 ± 3	3	303	-2	98
Cu	301 ± 3	3	295	2	102
Pb	310 ± 6	3	(305)**	2	102

*Number of separate digestions and analysis.
**Values in parentheses are noncertified concentrations.

Table 6. Analytical Sensitivity and Minimum Concentration Level (MCL) of SRM 1083 (Base Oil) by Microwave Digestion and Flame AA Analysis.

SRM 1083 (Base Oil)			
Element (Values in μg/g)	Analytical Sensitivity*	Minimum Concentration**	Certified Value
Al	0.35	<32	<0.5
Fe	0.07	< 7	1.0
Ni	0.07	4	<0.4
Cu	0.05	< 4	<0.5
Pb	0.3	<29	<0.04

*AA Sensitivity at 2 X Scale Expansion.
**MCL obtained by the following equation:

$$\frac{\text{Sensitivity } (\mu g/g) \times 50 \text{ mL dilution}}{\text{wt of oil (g)}} = \text{MCL (Element)}$$

The two microwave heating programs run in this study were longer than the one referenced in the CEM Corporation manual (Table 1). These procedures were not optimized to give the shortest digestion time but were run longer to ensure a complete dissociation of metals from the oil. The manufacturer's total digestion time (heating and cooling) was 60 min compared to 80 min during this study.

A comparison of the percent relative error and percent recovery between the 100-ppm and 300-ppm SRM shows a more consistent recovery and improved accuracy for the 300-ppm SRM (Tables 4 and 5). Because the metals were analyzed using flame AA, some metals (e.g., lead) were at their lower sensitivity level at the 100-ppm level. Improved recovery for the 100-ppm SRM may have occurred using a furnace technique; however, furnace is much slower than flame analysis.

The presence of undigested particles did not affect the percent recovery of metals in oil except perhaps in the lower recovery of Pb in the 100-ppm wear-metal samples. The oil was not completely digested because organic materials do not totally decompose to CO_2 and H_2O by nitric acid.[5] Although not performed in this study, the drop-wise addition of 30% hydrogen peroxide to the samples may have completed the reaction.[3]

Extraction of metals in oil can often be done quicker using a solvent extraction technique (typically xylene or kerosene) as opposed to matrix destruction. However, the solvent extraction technique suffers the disadvantage of requiring the use of organometallic standards, as well as the fact that it is not a particle size independent technique. The closed vessel microwave digestion technique can be performed using aqueous standards, and this technique is particle size independent. Thus, the preferred extraction technique will depend upon the nature of the sample (particle size), as well as the availability of materials (solvents, speciality standards).

5. CONCLUSIONS

Closed vessel microwave acid digestion is a relatively quick matrix destruction technique for the determination of wear metals in oil. Typically, 12 samples can be completely digested in approximately 60-80 min. Atomic absorption analysis for Al, Fe, Ni, Cu, and Pb from the National Bureau of Standards Standard Reference Materials showed recoveries using this technique. Recoveries ranged from 98 to 103% for the 300-ppm wear metals in oil. The 100-ppm wear metals in oil had three metals with recoveries ranging from 99 to 103% and two metals with outlier recoveries 84% (Pb) and 110% (Fe).

Blank

LITERATURE CITED

1. Brown, J.R., Saba, C.S., and Rhine, W.E., "Particle Size Independent Spectrometric Determination of Wear Metals in Aircraft Lubricating Oils," Anal. Chem. Vol. 52 (14), pp 2365-2370 (1980).

2. Kauffman, R.E., Saba, C.S., and Rhine, W.E., "Quantitative Multielement Determination of Metallic Wear Species in Lubricating Oils and Hydraulic Fluids," Anal. Chem. Vol. 54 (6), pp 975-979 (1982).

3. Gilman, L.B., General Guidelines for Microwave Sample Preparation, pp 1-85, CEM Corporation, Matthews, NC, 1988.

4. Kingston, H.M., and Jassie L.B., "Microwave Energy for Acid Decomposition at Elevated Temperatures and Pressures Using Biological and Botanical Samples," Anal. Chem. Vol. 58 (12), pp 2534-2541 (1986).

5. Bock, R., A Handbook of Decomposition Methods in Analytical Chemistry, Translated and Revised by I.L., Marr, Wiley, New York, NY, 1979.